

**DYNAMIC OPTIMIZATION OF LOW DENSITY
POLYETHYLENE PRODUCTION IN TUBULAR
REACTOR UNDER THERMAL SAFETY AND
FOULING RESISTANCE CONSTRAINTS**

ASHRAF BIN AZMI

UNIVERSITI SAINS MALAYSIA

2019

**DYNAMIC OPTIMIZATION OF LOW DENSITY POLYETHYLENE
PRODUCTION IN TUBULAR REACTOR UNDER THERMAL SAFETY
AND FOULING RESISTANCE CONSTRAINTS**

by

ASHRAF BIN AZMI

Thesis submitted in fulfillment of the requirements

For the degree of

Doctor of Philosophy

August 2019

ACKNOWLEDGEMENTS

In the name of Allah, The Most Gracious and the Most Merciful

All praises to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisors, Associate Professor Dr. Norashid bin Aziz and Dr. Suhairi Bin Abdul Sata for their patience, suggestion, supervision and constant support to me in accomplishing this research.

I would like to express my appreciation to the School of Chemical Engineering (SCE) Dean, Professor Ir. Dr. Zainal Ahmad for his support and help towards my postgraduate affairs. My acknowledgement also goes to all technicians and office staffs of SCE for their co-operations. My outmost appreciation goes to PETRONAS Chemicals LDPE Sdn. Bhd staff particularly Mrs. Norazilwati, Mr. Fadzli Wahab and Mrs. Norfadhillah Abdullah for their kind co-operation and guidance. The financial support from Ministry of Higher Education Malaysia (MOHE) through Mybrain 15 Scheme, and Universiti Sains Malaysia through Research University Grant Scheme (1001/PJKIMIA/814237) and Fundamental Research Grant Scheme (203/PJKIMIA/6071368) are greatly acknowledged.

This work is dedicated to my beloved mother, Datin Hj. Siti Hajar Binti Haji Isa, my late father, Allahyarham Dato' Dr. Hj. Azmi Bin Hj. Ahmad, and my beloved wife, Dr. Iylia Binti Idris for their endless loves, prayers, and encouragements. Also not forgetting my parents in law Ir. Hj. Idris Bin Abu Bakar and Hj. Fadziyah Binti Yahaya. I would like to thank my siblings Dr. Najib, Ir. Farid, Sir Faiz, Ir. Ikram and Captain Hatim.

A special appreciation to my closest friends Dr. Fakhrony Sholahudin, Dinie, Nazarudin, Asyura, Nurazimah, Jamaludin, Sudibyo, Ehsan Zhalehrajabi, Hafizul, Wong Mo Keong, Suthakaran and others for their kindness, help, financial and moral support during my study. To those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much.

Ashraf Bin Azni, PhD Journey (2015-2019)

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	x
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xvi
LIST OF SYMBOLS	xix
ABSTRAK	xxiv
ABSTRACT	xxvi
CHAPTER ONE: INTRODUCTION	
1.1 Research Background	1
1.2 Problem Statement	5
1.3 Research Objectives	8
1.4 Thesis Outline	8
CHAPTER TWO: LITERATURE REVIEW	
2.1 Production of LDPE in Industrial High Pressure Tubular	11
2.2 The Importance of Optimization Study in LDPE Tubular Reactor	15
2.3 Optimization Studies on LDPE Production in Tubular Reactor	17

2.4	Thermal Safety (T_{cm}) and Fouling Resistance (R_{fm})	25
	Constraints Consideration in Optimization	
2.5	Dynamic Optimization of LDPE Tubular Reactor	26
2.6	LDPE Tubular Reactor Modeling	27
2.6.1	Reaction Mechanism	28
2.6.1(a)	Initiation	34
2.6.1(b)	Propagation	36
2.6.1(c)	Termination	37
2.6.1(d)	Chain Transfer	38
2.6.1(e)	Backbiting and β -Scission	38
2.6.2	Pressure Pulse and Axial Mixing	39
2.6.3	Single Phase Assumption	40
2.6.4	Kinetic Rate Parameters	40
2.6.5	Product Properties	43
2.6.6	Thermal Safety Analysis	44
2.6.7	Fouling Resistance	47
2.7	Solution Methods of Dynamic Optimization Problems	49
2.7.1	Classical Variation Methods	49
2.7.2	Dynamic Programming	49
2.7.3	Discretization Techniques	50
2.8	Concluding Remarks	53

CHAPTER THREE: MATERIALS AND METHODS

3.1	Low Density Polyethylene Production in Industrial High Pressure	56
	Tubular Reactor Process Overview	

3.2	Data Collection	60
3.3	Model Development	61
3.3.1	Tubular Reactor Configuration	61
3.3.2	Model Formulation and Assumptions	63
3.3.3	Reaction Mechanisms	65
3.3.3(a)	Main Reactions	66
3.3.3(b)	Side Reactions	66
3.3.4	Model Equations and Property Correlation	67
3.3.4(a)	Mass Balance of Components in the Tubular Reactor	68
3.3.4(b)	Energy Balance in the Tubular Reactor	69
3.3.4(c)	Momentum Balance	69
3.3.4(d)	Live Radical Model	69
3.3.4(e)	Polymer Model	70
3.3.4(f)	Reacting Mixture Density	71
3.3.4(g)	Heat Capacity	72
3.3.4(h)	Heat Transfer Coefficient	73
3.3.4(i)	Property Correlations of Plant Outputs	73
3.3.4(j)	Kinetic Rate Constants	74
3.3.4(k)	Initiation Rate Efficiency	75
3.3.4(l)	Kinetic Rate Constants Parameter Estimation	75
3.3.4(n)	List of Parameters to be Estimated	78
3.4	Model Validation and Sensitivity Analysis	82
3.4.1	Comparison of simulations result and industrial data	82
3.4.2	Model Input – Output Sensitivity Study	85

3.5	Fouling Resistance Study	86
3.5.1	Overall Heat Transfer Coefficient via Correlation	86
3.5.2	Determination of Fouling Resistance using Plant Data	88
3.6	Thermal Safety Analysis	89
3.6.1	Adiabatic Temperature Rise	89
3.6.2	Assessment Criteria for the Severity of a Runaway Condition	90
3.6.3	Reaction Temperature under Critical Condition (T_c)	91
3.7	Dynamic Optimization	92
3.7.1	Define the Input Arguments	94
3.7.2	Optimization Problem Formulation	96
3.7.3	Execution of Dynopt Code	97
3.7.4	Different Objective Functions Study	99
3.8	Case Studies	101
3.8.1	Case 1 (A): Unconstrained Optimization Problem	104
3.8.2	Case 1 (B): Max. Conversion under Reactor Temperature Constraint	105
3.8.3	Case 1 (C): Max. Conversion with Reaction Critical Temperature Constraint	105
3.8.4	Case 1 (D): Max. Conversion with Fouling Resistance Constraint	106
3.8.5	Case 1 (E): Max. Conversion with Product Grade Constraint	107
3.8.6	Case 1 (F): Max. Conversion with Side Products Constraint	107
3.8.7	Case 1 (G): Max. Conversion using Selected Constraints	108

3.8.8	Case 2: Min. Side Products Objective Function	109
3.8.9	Case 3: Min. Fouling Resistance	110
3.8.10	Case 4: Min. Compression Power (CP)	110
3.8.11	Case 5: Max. Profit	111
3.9	Number of Intervals Effect on LDPE Tubular Reactor Performance	112
3.10	Summary	112

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Kinetic Parameter Estimation and Model Validation	113
4.2	Overall Heat Transfer Coefficient	120
4.3	Fouling Resistance	124
4.4	Thermal Safety Constraint	128
4.5	Effect of process parameter on performance and quality of LDPE Tubular Reactor Polymerization	132
4.5.1	Effect of Initiator, Monomer and Solvent Feed Flow Rate on Reactor T and XM	132
4.5.2	Effect of Initiator, Monomer and Solvent Feed Flow Rate on LDPE Properties	134
4.5.3	Effect of Jacket Temperature and Inlet Pressure on Reactor Temperature and Monomer Conversion	138
4.5.4	Effect of Jacket Temperature and Inlet Pressure on Product Quality	140
4.5.5	Analysis on the Effect of Process Parameters on Reactor Performance	143

4.6	Dynamic Optimization of Tubular Reactor	144
4.6.1	Maximize Conversion using Different Constraints: Case 1	144
	(A) – Case 1 (G)	
4.6.1(a)	Case 1 (A): Unconstrained Optimization	148
4.6.1(b)	Case 1 (B - C): Reaction Temperature and Critical Temperature Constraint	154
4.6.1(c)	Cases 1 (D - G): Fouling Resistance, Product Grade, Side Product Content, and Combination of Constraints	159
4.6.2	Comparison of Different Objective Functions	164
4.6.3	Number of Interval Effect on LDPE Tubular Reactor Performance	171

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	175
5.2	Recommendations	179

REFERENCES	180
-------------------	-----

APPENDICES

Appendix A

Appendix B

Appendix C

LIST OF PUBLICATIONS

LIST OF TABLES

	Page
Table 2.1 Optimization works in the LDPE tubular reactor	22
Table 2.2 All the major research work existed in the LDPE study, plus the research work that is proposed in the present study	29
Table 3.1 Lists of all the available/unavailable data from PCLDPE plant with its respective allocation.	59
Table 3.2 List of the values used in this parameter estimation study (Yao, 2004) and unknown parameters	77
Table 3.3 Lower and upper bounds of the estimated parameters	78
Table 3.4 Details of the PCLDPE tubular reactor studied	80
Table 3.5 Industrial data for the output measurement of LDPE tubular reactor	81
Table 3.6 Assessment criteria for the severity of a runaway condition	87
Table 3.7 List of constraints used in optimization	92
Table 3.8 Cost of product price, raw materials and utility cost	96
Table 3.9 List of case studies involved in the dynamic optimization study	98
Table 4.1 Values of estimated values of frequency factor (A_x)	109
Table 4.2 Comparison of the model predicted values to the industrial data	111
Table 4.3 Overall heat transfer coefficient obtained by correlation and plant data	116
Table 4.4 Effect of process parameters of reactor performance	137

Table 4.5	Result for Maximize Conversion OF using different constraints	139
Table 4.6	Optimal value of parameter variables (p_x) for Maximize Conversion OF with different constraints study	140
Table 4.7	Dynamic optimization result for different OF studies	160
Table 4.8	Optimal input parameter for different OF studies	161
Table 4.9	The optimization results for different number of intervals	166

LIST OF FIGURES

		Page
Figure 2.1	Schematic diagram of an industrial LDPE tubular reactor (Agrawal, 2007)	12
Figure 2.2	Simplified flow sheet of LDPE plant	14
Figure 2.3	The runaway scenario (Gygax, 1988), showing the adiabatic temperature rise of the synthesis reaction (T_{ad}) after a cooling failure from the process temperature (T_r) to the highest temperature reached.	45
Figure 3.1	Flowchart of methodologies adopted in this study	54
Figure 3.2	Simplified flow diagram of the PCLDPE high pressure tubular reactor	56
Figure 3.3	A simplified tubular reactor configuration	60
Figure 3.4	Dimension of each pipes in tubular reactor in millimeter	61
Figure 3.5	Flow stream of reaction mixture and jacket in a tubular reactor	61
Figure 3.6	Parameter estimation procedure	76
Figure 3.7	Flowchart of the dynamic optimization procedure	90
Figure 4.1	Reaction temperature trajectories of model and industrial data	110
Figure 4.2	XM trajectories of model and industrial data	110
Figure 4.3	Trajectories of model's weight-average molecular weight (MW) across LDPE tubular reactor	113

Figure 4.4	Trajectories of model's short chain branch per 1000 atom CH ₂ across LDPE tubular reactor	114
Figure 4.5	Trajectories of model's vinyl groups per 1000 atom CH ₂ across LDPE tubular reactor	114
Figure 4.6	Trajectories of model's vinylidene groups per 1000 atom CH ₂ across LDPE tubular reactor	115
Figure 4.7	Heat transfer coefficient, U (Method 2) of different production time as a function of axial length of tubular reactor	118
Figure 4.8	R_f as a function of axial length of tubular reactor	119
Figure 4.9	R_f of the fourth cooling zone, over the period of ten hours	121
Figure 4.10	Reactor temperature (T) profile under normal operating condition of Base Case (reference model) across the tubular reactor	124
Figure 4.11	Reaction critical temperature (T_c) profile of Base Case (reference model) across the tubular reactor	125
Figure 4.12	Effects of: a) F_I on reactor T ; b) F_I on XM ; c) F_M on reactor T ; d) F_M on XM ; e) F_S on reactor T ; and f) F_S on XM	127
Figure 4.13	Effects of: a) F_I on MW ; b) F_I on content of SCB /1000CH ₂ ; c) F_I on $V_i/1000CH_2$; and d) F_I on $V_{id}/1000CH_2$	129
Figure 4.14	Effects of: a) F_M on MW ; b) F_M on content of SCB /1000CH ₂ ; c) F_M on $V_i/1000CH_2$; and d) F_M on $V_{id}/1000CH_2$	131
Figure 4.15	Effects of: a) F_S on MW ; b) F_S on content of SCB /1000CH ₂ ; c) F_S on $V_i/1000CH_2$; and d) F_S on $V_{id}/1000CH_2$	132
Figure 4.16	Effects of: a) T_J on reactor T ; and b) T_J on XM	133

Figure 4.17	Effects of: a) P_{in} on reactor T ; and b) P_{in} on XM	134
Figure 4.18	Effects of a) T_J on MW; b) T_J on content of SCB /1000CH ₂ ; c) T_J on V_i /1000CH ₂ ; and d) T_J on V_{id} /1000CH ₂	135
Figure 4.19	Effects of a) P_{in} on MW; b) P_{in} on content of SCB /1000CH ₂ ; c) P_{in} on V_i /1000CH ₂ ; and d) P_{in} on V_{id} /1000CH ₂	136
Figure 4.20	Comparison of reactor jacket temperature profile of Base Case (reference model) and unconstrained optimization (Case 1A)	141
Figure 4.21	Comparison of reactor jacket temperature profile of Cases 1(A) – (C)	142
Figure 4.22	Comparison of T_J of Cases 1 (C) – (G)	141
Figure 4.23	Monomer conversion profile of Base Case (reference model) and unconstrained optimization (Case 1A)	143
Figure 4.24	Comparison of reactor temperature profile of Base Case (reference model) and unconstrained optimization (Case 1A)	143
Figure 4.25	Reactor critical temperature profile of Base Case (reference model) and unconstrained optimization (Case 1A)	144
Figure 4.26	Fouling resistance across tubular reactor of Base Case (reference model) and unconstrained optimization (Case 1A)	144
Figure 4.27	Monomer conversion profile of Base Case, Case 1(B) and Case 1(C)	149
Figure 4.28	Comparison of reactor temperature profile of Base Case, Case 1(B) and Case 1(C) across the tubular reactor	149

Figure 4.29	Comparison of reactor critical temperature profile of Base Case, Case 1(B) and Case 1(C) across the tubular reactor	150
Figure 4.30	Fouling resistance comparison of Base Case, Case 1(B) and Case 1(C) across the tubular reactor	150
Figure 4.31	Monomer conversion profile of Cases 1(C) – (G) across the tubular reactor	154
Figure 4.32	Comparison of reactor temperature profile of Case 1(C) - (G) across the tubular reactor	154
Figure 4.33	Comparison of reactor critical temperature profile of Cases 1(C) - (G) across the tubular reactor	155
Figure 4.34	Fouling resistance comparison of Cases 1(C) - (G) across the tubular reactor	155
Figure 4.35	Comparison of reactor jacket temperature profiles across the tubular reactor for Case 1(G) and Cases (2 – 5)	162
Figure 4.36	Monomer conversion profiles across the tubular reactor for Case 1(G) and Cases (2 – 5)	163
Figure 4.37	Comparison of reactor temperature profiles across the tubular reactor for Case 1(G) and Cases (2 – 5)	163
Figure 4.38	Comparison of reactor critical temperature profiles across the tubular reactor for Case 1(G) and Cases (2 – 5)	164
Figure 4.39	Fouling resistance profiles across the tubular reactor for Case 1(G) and Cases (2 – 5)	164
Figure 4.40	Optimal reactor jacket temperature trajectories for various number of interval	167

LIST OF ABBREVIATIONS

CH ₂	Methylene
CP	Compression Power
CPU	Computer processor unit
CTA	Chain transfer agent
CVI	Control vector iteration
CVP	Control vector parameterization
DAE	Differential algebraic equation
FD	Finite Difference
GDP	Gross domestic product
HJB	Hamilton–Jacobi–Bellman
HP	High pressure
IDP	Iterative dynamic programming
IVP	Initial value problem
JG	Jumping gene
LDPE	Low density polyethylene
LP	Low pressure
MFI	Melt flow index
Me	Methyl
MW	Molecular weight
NCO	Necessary conditions optimality

NLP	Non-linear programming
NSGA-II	Non-dominated sorting genetic algorithm
OC	Orthogonal collocation
ODE	Ordinary differential equation
OI	Oxygen initiation
PCLDPE	PETRONAS Chemicals Sdn. Bhd.
PMP	Pontryagin's Minimum Principle
PI	Peroxide initiation
PRO	Chain propagation
QN	Quasi-Newton
R	Regression
Re	Reynolds number
SCB	Short chain branches
SP	Side products
SQP	Sequential quadratic programming
SSE	Sum square of error
TC	Termination by combination
TD	Termination by disproportionation
TDT	Thermal degradation
THI	Thermal initiation

TM	Chain transfer to monomer
TP	Chain transfer to polymer
TS	Chain transfer to solvent
TPBVP	Two-point boundary value problem
V_i	Vinyl group
V_{id}	Vinylidene group
XM	Monomer conversion
ZHA	Zurich Hazard Analysis

LIST OF SYMBOLS

A_i	Inside pipe area	cm ²
A_o	Outside pipe area	cm ²
$A_{x,i}$	Frequency factor of x process with i -th number	l/s; cm ³ /mol.s
bb	Backbiting	-
$C_{x,i}$	Concentration x component with i -th number	mol/cm ³
D	Diameter	cm
D_{in}	Inside diameter of reactor,	cm
D_e	Equivalent diameter	cm
D_{ji}	Inner diameter of jacket wall	cm
$E_{x,i}$	Activation energy of x process with i -th number	cal/mol
e	Ethylene	-
F_x	Mass flow rate of x component	kg/h
f_x	Initiation efficiency of x -th peroxide	-
f_r	Fanning friction factor	-
G_c	Jacket volumetric flux rate	cm ³ .cm ⁻² .s ⁻¹
h_i	Reactor side heat transfer coefficient	cal/cm ² .s.K
h_o	Outside film heat transfer coefficient	cal/cm ² .s.K
h_w	Heat transfer coefficient of reactor wall	cal/cm ² .s.K
$K_{d,i}$	Rate constant of peroxide initiation with i -th number	l/ s

K_{th}	Rate constant of monomer thermal initiation,	l/ s
K_p	Rate constant of propagation,	l/mol.s
K_{td}	Rate constant of termination by thermal degradation	l/mol.s
K_{thd}	Rate constant of termination by disproportionation	l/mol.s
K_{trm}	Rate constant of chain transfer to monomer	l/mol.s
K_{trp}	Rate constant of chain transfer to polymer	l/mol.s
K_{trs}	Rate constant of chain transfer to solvent	l/s
K	Rate constant of -scission to secondary radical	l/s
K_1	Rate constant of -scission to tertiary radical	l/s
K_m	Thermal conductivity of reaction mixture	cal/cm.s.K
K_w	Thermal conductivity of reactor wall	cal/cm.s.K
K_J	Thermal conductivity of jacket water	cal/cm.s.K
L	Length of reactor [IE2:S,1]	cm
I	Initiator	-
M	Monomer	-
m	Reaction mixture	-
\dot{m}_x	Mass flow rate of x-th component	g/s
Nu	Nusselt number	-
P	Reaction pressure	Bar
pe	Polyethylene	-

P_{in}	Reactor inlet pressure	Bar
Pr	Prandtl number	-
p_x	Input variable of x component	
$P(x)$	Dead polymer with chain length x	-
Q	Heat transfer	Joules
r_o	Outside radius of tubular reactor area	cm
r_i	Inside radius tubular reactor area	cm
R	Ideal gas constant	cal/mol.K
$R(x)$	Live radical with chain length x	-
Re	Reynolds number	-
R_f	Fouling resistance	cm ² . s.K /cal
R_{fm}	Maximum fouling resistance	cm ² . s.K /cal
S	Solvent	-
T	Temperature	C
T_{in}	Reactor inlet temperature	C
T_J	Reactor jacket temperature	C
T_{max}	Maximum reaction temperature	C
T_{cm}	Maximum reaction critical temperature	C
T_{cp}	Peak critical temperature	C
U	Overall heat transfer coefficient,	cal/cm ² .s.K
u_x	Control variable of x component	

v	Linear velocity of the reaction mixture in reactor	cm/s
V_i	Vinyl group	
V_{id}	Vinylidene group	
V_m	Specific volume of monomer	cm ³ /g
V_p	Specific volume of polymer	cm ³ /g
$V_{x,i}$	Activation volume of x component with i -th number	l/mol
X_M	Monomer conversion	%
z	Axial distance from reactor inlet	cm

Greek Symbols

H_p	Heat of polymerization	cal/mol
T_{ad}	Adiabatic temperature rise	°C
T_{l1}	Log mean temperature	-
λ_x	x -th moment of the live polymer radical	-
μ_x	x -th moment of dead polymer radical	-
	Beta scission of secondary radical	-
I	Beta scission of tertiary radical	-
\emptyset	Diameter	
	Reaction mixture density	g/cm ³
s	Viscosity of reactant mixture	Poise
r	Relative viscosity of monomer	Poise

ν	Viscosity of monomer	Poise
ν	Viscosity of reaction	Poise
w_m	Weight fraction of monomer	-
w_p	Weight fraction of polymer	-